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Low dissipation-factor fluorocarbon resins and cabl s pr pared th r from.

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Abstract

A coaxial cable having foamed or unfoamed insulation consisting essentially of a melt processable copolymer of tetrafluoroethylene and less than about 11.5% of a comonomer, said copolymer being fluorinated at elevated temperature after polymerization, has improved electrical properties over a broad frequency range.

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⑫ **EUROPEAN PATENT APPLICATION**

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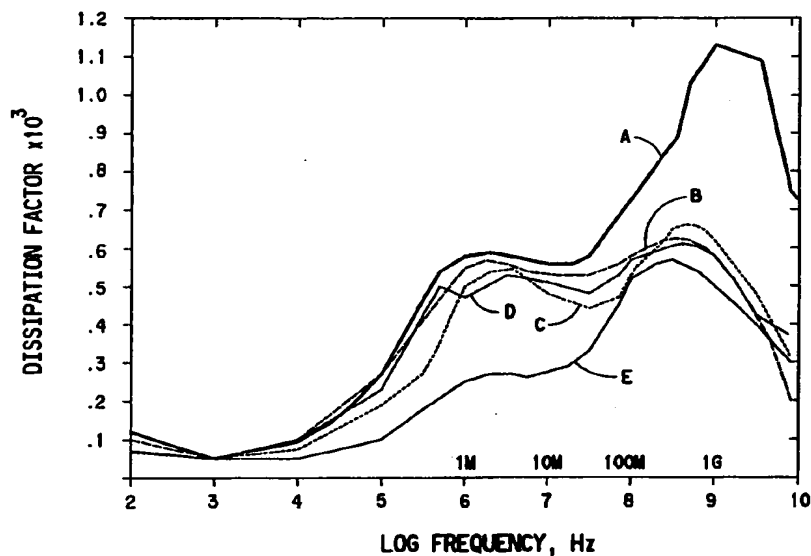
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㊼ Low dissipation-factor fluorocarbon resins and cables prepared therefrom.

㊽ A coaxial cable having foamed or unfoamed insulation consisting essentially of a melt processable copolymer of tetrafluoroethylene and less than about 11.5% of a comonomer, said copolymer being fluorinated at elevated temperature after polymerization, has improved electrical properties over a broad frequency range.

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FIG.1

LOW DISSIPATION-FACTOR FLUOROCARBON RESINS AND CABLES PREPARED THEREFROM

BACKGROUND OF THE INVENTION

5   This invention relates to insulated cables having improved electrical insulation properties over a wide range of frequencies.

Fluorocarbon resins are used as electrical insulators, particularly for low-loss coaxial cables and other high-frequency transmission media or circuit components. Copolymers of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), for example, have been used in such applications. Although such copolymers have excellent high-temperature properties and environmental resistance, the electrical properties, particu-

10   larly the dissipation factors, of such resins are not as good as would be desired for cables to be used in certain microwave and radio frequency applications. The present invention, therefore, provides a cable with improved high frequency transmission properties over a broad range of frequencies.

U.S. Patent 4,560,829 discloses a coaxial cable in which the electrical insulation is a fluoropolymer such as a tetrafluoroethylene copolymer . The copolymer is preferably one which has a loss tangent less than

15   0.0010 at 10 GHz, and can be TFE/HFP copolymer or a copolymer of TFE with perfluoroalkoxyalkene. The fluoropolymer is foamed using a foaming agent having the formula C_nF_{2n+2}.

U.S. Patent 4,626,587, Morgan et al., discloses a process for reducing the backbone instability of a copolymer of TFE and HFP, by subjecting the copolymer to high shear in a twin-screw extruder. Thereafter the pellets obtained are exposed to fluorine gas to improve the color and eliminate the remaining unstable .

20   endgroups.

U.S. Patent 4,743,658, Imbalzano et al., discloses a copolymer of TFE and perfluoro(alkyl vinyl) ether substantially free of unstable end groups. The unstable end groups are virtually eliminated by treatment of the polymer with fluorine from a variety of fluorine radical generating compounds, preferably fluorine gas, optionally diluted with an inert gas such as nitrogen.

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SUMMARY OF THE INVENTION

30   The present invention provides an elongate article comprising at least one elongate metallic conductive element and an elongate insulator contacting the conductor and consisting essentially of at least one melt processible copolymer of tetrafluoroethylene with at least one copolymerizable perfluorinated comonomer other than tetrafluoroethylene in an amount less than about 11.5% based on the weight of the copolymer and sufficiently low that the melting point of the copolymer is at least about 250° C, said copolymer being

35   fluorinated at elevated temperature after polymerization.

BRIEF DESCRIPTION OF THE FIGURE

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The Figure shows dissipation factor as a function of frequency for a number of resins of the present invention.

45   ## DETAILED DESCRIPTION OF THE INVENTION

The polymers useful in preparing the cables of the present invention are melt processible fluoropolymers based on tetrafluoroethylene (TFE) as the predominant monomer. Although poly-

50   tetrafluoroethylene (PTFE) itself has excellent electrical properties, it is not generally suitable for use in electrical cable applications because it is not melt processible. Nevertheless, incorporation of minor amounts of comonomers can result in a copolymer which is melt processible and which retains many of the desirable electrical and thermal properties of PTFE. The polymer of the present invention is based on such a copolymer of TFE and a perfluorinated comonomer. Suitable comonomers include perfluoroalkenes of the formula $R_FCF=CF_2$ where R_F is a perfluoroalkyl group having 1-5 carbon atoms, such as h x-

afluoropropylene; perfluoro(n-alkyl vinyl) ethers wherein the alkyl group has 1 to 5 carbon atoms; and mixtures thereof. Preferably the n-alkyl group is propyl. Of course, blends of such polymers may be equally well used.

5 The amount of the comonomer or comonomers pr sent should be sufficient to provide a copolymer which is melt proc ssible, but not so much that the copolymer loses significant structural or electrical properties. Loss of structural properties is related to the reduction of melting point and molecular weight which occurs upon addition of such comonomers, and will, of course, vary with the amount and identity of the comonomer. Those with longer chains will have a larger effect on the melting point than those with shorter chains. The amount of comonomer added should be low enough that the melting point of the
10 copolymer is not reduced below about 240° C, and preferably not below about 260-270° C. As illustration, a copolymer of TFE and 12.3 % HFP has a melting point of about 260-270° C; a copolymer of TFE and 3.9% perfluoro(propyl vinyl ether) (PPVE) has a melting point of about 308° C. When the comonomer is PPVE, therefore, it is preferable that the amount of PPVE be less than about 5%.

In addition to considerations of thermal performance, the amount of the comonomer should be limited in
15 order to retain superior electrical performance over a broad frequency range. It has been found that when the amount of comonomer is less than about 11.5%, and preferably less than about 11% by weight, the dissipation factor of the resin is improved, as compared to resins having higher comonomer levels.

When the comonomer is HFP, the actual level of comonomer can be estimated by measuring the ratio of the intensity of the infrared absorption at 982 cm^{-1}, associated with the HFP comonomer, to the intensity
20 of the absorption at 2367 cm^{-1}. Commercial TFE-HFP copolymer containing about 12.3 weight % HFP exhibits a ratio of 3.75 to 3.95. A ratio of 3.6 corresponds approximately to 11.5 weight percent; a ratio of 3.4 corresponds to about 10.9 percent, and so on. Thus for TFE-HFP copolymers, this IR ratio should be less than about 3.6, preferably less than about 3.4. Alternatively, the comonomer content can be measured using F19 NMR spectroscopy.

25 When the comonomer is PPVE (or a mixture of PPVE with other comonomers), the PPVE should be present in an amount of about 5% or less, as stated above. This limit provides both adequate physical and thermal properties and superior electrical properties. Preferably the PPVE comonomer should be present in an amount of about 4% or less.

When the comonomer is a mixture of HFP and PPVE, it is preferred that the total amount of the two
30 comonomers is less than about 8% by weight and the amount of the HFP is less than about 6% by weight.

The improvement in dissipation factor which is achieved by limiting the amount of comonomer is most apparent at comparatively low frequencies, in the 1 MHz region. (1 MHz = 10^6 cycles per second.) For transmission of e.g. television signals, however, the frequency region of 100 MHz to 10 GHz is also important. It has been found that treatment of the copolymers defined above with fluorine greatly reduces
35 the dissipation factor at such higher frequencies. Although not intending to be bound by any theory, it is believed that such a fluorination step converts various functional end groups of the copolymer to -CF$_3$ groups. It is believed that it is the functional end groups that are responsible for much of the dielectric loss at high frequencies in the untreated polymer. Therefore an important part of the present invention is the fluorination of the polymer after polymerization in order to remove substantially all of these groups. A level
40 of about 50 end groups other than -CF$_3$ per million carbon atoms can be reasonably detected by infrared spectroscopy, as described in more detail in U.S. Patent 4,675,380, the disclosure of which is incorporated herein by reference. Thus the polymer should have fewer than about 50 and preferably fewer than about 20 such groups per million carbon atoms.

The fluorination process is normally conducted at elevated temperatures, in order to permit complete
45 reaction of end groups. (Temperature above room temperature is believed to permit diffusion of fluorine into the structure of the polymer to permit encounter with the end groups.) Temperatures of at least 200° C are normally used. But the temperature should preferably be below the softening temperature of the polymer, in order to avoid problems with agglomeration. Fluorination may be performed by treatment with gaseous fluorine, either alone or in comixture with an unreactive gas, such as nitrogen, or by the use of an alternative
50 fluorination agent. The polymer, during the fluorination process, may be in the form of pellets, beads, porous beads, or fluff. Suitable fluorination processes are described in more detail in U.S. Patent 4,743,658, the disclosure of which is incorporated herein by reference.

The presence of terminal groups such as -CF$_2$H can also be avoided by means other than post-polymerization fluorination. For example, in the polymerization process itself, initiators can be used which
55 provide a terminal -CF$_3$ group under appropriate conditions. Examples of such initiators include fluorine (F$_2$), difluorodiazine (N$_2$F$_2$), perfluoroalkyl peroxides such as CF$_3$-(CF$_2$)$_n$-O-O-(CF$_2$)$_m$-CF$_3$, as reported by R. S. Porter and G. H. Cady in the Journal of the American Chemical Society, 79 , 5638 (1955), perfluoroacyl peroxides such as (CF$_3$-(CF$_2$)$_n$-COO)$_2$, as reported in U.S. Patent 3,528,952, perfluoroacyl hypofluorites

such as F-(CF$_2$)$_n$-COOF, as r port d in U.S. Pat nt 4,588,796, th reaction product of hexafluorpropylene trimers and fluorine, ((CF$_3$)$_2$CF)$_2$(CF$_3$CF$_2$)C$\cdot$, as disclosed in U.S. Patent 4,626,608, perfluoroacyl peroxides based on hexafluoropropylene oxide, (C$_3$F$_7$-O-CF(CF$_3$)-COO)$_2$ with C$_3$F$_7$ groups either linear or branched, as disclosed by Z. Chengxue et al. in the Journal of Organic Chemistry, 47 , 2009 (1982), difluoramines such as C$_3$F$_7$-C(CF$_3$)$_2$NF$_2$, perfluorazo compounds such as ((CF$_3$)$_2$CFN)$_2$, perfluorosulfonyl azides such as CF$_3$SO$_2$N$_3$, perfluoro acid chlorides such as C$_3$F$_7$COCI, perfluoroalkyl hypofluorites such as CF$_3$OF, and so on.

Resins such as these with improved dissipation factors over a broad frequency range are useful as wire and cable coating compositions, and are particularly useful as insulation in coaxial cables, the construction of which is well known. A coaxial cable comprises a central conductive element or wire, usually of a metal such as copper. The central element is surrounded by an insulating medium, which in turn is surrounded by an outer conductive element, which may be, for example, a metallic foil, a woven or braided composite wire, or a drawn aluminum, copper, or other metallic tube. The outer conductive element can also be encased in further protective insulation.

Coaxial cables can be prepared by melt extruding around a central conductor a foamable polymer composition of at least one of the fluorinated polymers described above, preferably with a foaming agent such as nitrogen or a chlorofluorcarbon such as CF$_2$HCl and optionally other traditional additives such as boron nitride. The extrusion is conducted at a temperature sufficient to cause the foaming agent to expand after the polymer exits the extruder die, thus providing a foamed core insulation about the central conductor. Thereafter an outer conductive metallic layer or shield is placed around the polymer layer. Preparation of coaxial cables with foamed core insulation components is described in more detail in U.S. Patent 3,072,583, the disclosure of which is incorporated herein by reference.

The present invention is also useful for preparing "twisted pairs" cables. These cables are similar to coaxial cables in that a central conductor is surrounded by low-loss insulation, except that a plurality, normally two, of such conductors are twisted together. There is optionally another conductor around the outside of the pair as a shield, as well as an overall insulating jacket.

Cables thus prepared using the specified polymers as insulation have improved electrical signal transmission properties. The attenuation of a signal upon passage through a coaxial cable is the sum of a loss due to the conductor material itself and the attenuation due to the dielectric loss of the core insulation. At high frequencies, the dielectric loss comprises an increasingly important fraction of the total attenuation, so the importance of minimizing dielectric loss due to the insulator is apparent. Insulator dielectric loss is proportional to the following relationship:

L = 0.092 x F x (DC)$^{\frac{1}{2}}$ x DF

where L is the dielectric loss in decibels per meter, F is the frequency in MHz, DC is the dielectric constant of the insulator, and DF is the dissipation factor. It is evident from this equation that insulation with a lower dissipation factor will provide cables with a lower overall dielectric loss, and this effect is be more pronounced at higher frequencies. It is just at these higher frequencies, i.e., 100 MHz and above, that the polymers of the present invention show the greatest improvement in dissipation factor. As a result, cables prepared from these resins show particularly improved transmission properties at high frequencies.

It is observed that use of foamed insulation for cables is often desirable, in order to take advantage of the superior insulator properties of air, i.e. its a dielectric constant of about 1.00 and dissipation factor of about 0. (Most solid homo- and copolymers of TFE have a dielectric constant of approximately 2.0-2.1.) Thus the effective dielectric constant and dissipation constant of a foamed polymer insulator are reduced proportionally to the void content. For this reason the use of foamed polymers, as described above, is an especially preferred embodiment of the present invention.

Comparative Example 1

A sample of commercial TFE-HFP copolymer, containing about 12.4% by weight HFP copolymer is examined. The copolymer is compression molded at 350°C into a film 0.1 mm thick and examined by infrared spectroscopy using a Nicolet Model 5DX Fourier transform infrared spectrometer. The ratio of the absorbance at 982 cm^{-1} to that at 2367 cm^{-1} ("IR ratio") is 3.85. The dissipation factor of this same resin is measured as a function of frequency on a plaque about 2.5 mm (0.1 inch) thick. The dissipation factor is measured by one or more methods, depending on the frequency of interest. Such methods are well known to those skilled in the art, and are described, for example, in "Dielectric Materials and Applications" by Arthur Von Hippel, MIT and Wiley & Sons, 1954, the disclosur of which is incorporated herein by r fer nce. For measurements from 1 kHz to 40 MHz, a capacitance bridge method is used, which is also

described in ASTM D 150. This method uses electrod s mounted on a micrometer for accurate dimensional det rminatiop. For m asurements from 40 MHz to 100 MHz, the reentrant cavity, susceptance variation method is used. For measurements from 135 MHz to 5 GHz, the standing wave method using a coaxial line is used. From 5 to 40 GHz the standing wave method in a circular hollow wave guide is used. The latter two
5 methods are also similar to procedures described in ASTM D-2520.

The results of these measurements are shown in Table I and in Figure 1 as curve A.

Example 1.

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A sample of TFE-HFP copolymer, having an IR ratio of 3.24, which corresponds to about 10.4 weight % HFP comonomer, is fluorinated as described in U.S. Patent 4,743,658, Example 1. Measurement of the dissipation factor as in Comparative Example 1 gave the results shown in Table I and Figure 1 (curve D). The combination of fluorination and reduced amount of HFP provides a material with significantly reduced
15 dissipation factor throughout the frequency range, particularly at higher frequencies.

Comparative Example 2

20 A polymer similar to that of Comparative Example 1, except having an IR ratio of about 3.75, is fluorinated as in Example 1. The results of measurement of the dissipation factor are shown in Figure 1 as curve B.

25 Comparative Examples 3 and 4.

Copolymers of TFE with 3.9 weight % PPVE, having a melt viscosity at 372° C of 4.25 x 10^4 poise (Comparative 3) or 2.2 x 10^4 (Comparative 4) are similarly tested. The results are shown in Table I. Although the dissipation factor at low frequencies is much better than that of Comparative Example 1, at
30 450 MHz and above there is little or no improvement.

Example 2.

35 The copolymer of Comparative Example 4 is fluorinated as in Example 1 and tested as above. The results are shown in Table I. The fluorine treatment reduces the dissipation factor at 450 MHz to about 42% of its original value.

40 Example 3.

A copolymer of TFE with 4.0 weight % HFP and 1.25 weight % PPVE is fluorinated as in Example 1 and tested as above. The results in Table I and Figure 1 (curve E) show excellent dissipation factors at all frequencies.

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TABLE I[1]							
		Dissipation Factor ($\times 10^4$)					
Ex.	Polymer	1 MHz	100 MHz	500 MHz	1 GHz	10 GHz
C1	TFE/12.4%HFP	5.73	7.20	10.20	11.20	8.40
1	TFE/10.4%HFP(Fl)	5.15	5.70	6.05	5.70	3.50
C3	TFE/3.9%PPVE	0.87	5.55	8.30	9.75	10.00
C4	TFE/3.9%PPVE	-	-	8.54[2]	-	-
2	TFE/3.9%PPVE(Fl)	-	-	3.66[2]	-	-
3	TFE/4.0%HFP/1.25%PPVE(Fl)	2.53	5.20	5.54	5.00	2.70

1. A hyphen (-) indicates that the measurement was not made. (Fl) indicates fluorine treatment.

2. measured at 450 MHz.

Example 4.

A copolymer of TFE with HFP, having an IR ratio of 3.5, obtained from Daikin (designated as NP-20), is fluorinated as in Example 1 and tested as above. The results, shown as Curve C in Figure 1, are similar to those of Example 1. The subtle differences in the details of the shapes of the two curves may be the result of different methods of manufacture, residual impurities, etc.

Example 5

The fluorinated polymer of Example 1 is melt extruded onto a 2.8 mm (0.109 inch) diameter copper wire using chlorodifluoromethane as the blowing agent and boron nitride as a nucleating agent, to form a foamed layer of insulation on the wire. The combined thickness of the wire plus insulation is 11.4 mm (0.450 inch). This operation is carried out according to the teaching of U.S. Patent 3,072,583. The foamed polymer has about 65% voids.

The cable thus made is shielded with aluminum foil in a manner known in the art. The total attenuation of the shielded cable is measured at different frequencies by using a high-frequency network analyzer according to standard measurement procedures. The dielectric attenuation is calculated from the total attenuation using the formula

$$A = (0.435/Z_0)(1/d + 1/D) (F)^{\frac{1}{2}} + 2.78P(K)^{\frac{1}{2}}F$$

where A is the total attenuation in decibels per 30.5 m (100 feet), the first term is the conductor attenuation, and the second term is the dielectric attenuation. Z_0 is the characteristic impedance, d is the diameter of the inner conductor and D is the outside diameter of the insulation layer both in units of 25.4 mm (inches), F is the frequency in megahertz, P is the power factor or dissipation factor, and K is the dielectric constant of the foam insulation. The cable so prepared exhibits significantly reduced dielectric attenuation over a wide spectrum of frequencies compared to similar cable prepared using the polymer of Comparative Example 1.

Claims

1. An elongate article comprising at least one elongate metallic conductive element and an elongate insulator contacting the conductor and consisting essentially of at least one melt processable copolymer of tetrafluoroethylene with at least one copolymerizable perfluorinated comonomer other than tetrafluoroethylene in an amount less than about 11.5% based on the weight of the copolymer and sufficiently low that the melting point of the copolymer is at least about 250° C, said copolymer being fluorinated at elevated temperature after polymerization.

2. An elongate article comprising at least one elongate metallic conductive element and an elongate

insulator contacting the conductor and consisting essentially of at least one melt processible copolymer of tetrafluoroethylene with at least one copolymerizable perfluorinated comonomer other than tetrafluoroethylene in an amount less than about 11.5% based on the weight of the copolymer and sufficiently low that th melting point of th copolymer is at least about 250°C, said copolymer having substantially exclusively -CF$_3$ end groups.

3. The article of claim 1 or 2 wherein the copolymer contains less than about 20 end groups other than -CF$_3$ per million carbon atoms.

4. The article of claim 1, 2 or 3 wherein the total amount of said additional comonomer is less than about 11% by weight.

5. The article of any one of claims 1 to 4 wherein the additional comonomer is selected from the group consisting of perfluoroalkenes of the formula $R_FCF=CF_2$ where R_F is a perfluoroalkyl group having 1-5 carbon atoms and perfluoro(n-alkyl vinyl) ethers wherein the alkyl group has 1 to 5 carbon atoms, and mixtures thereof.

6. The article of claim 5 wherein the additional comonomer is hexafluoropropylene or perfluoro(propyl vinyl ether).

7. The article of claim 5 wherein the additional comonomer is hexafluoropropylene.

8. The article of any one of claims 1 to 7 wherein the ratio of the absorbance of the copolymer at 982 cm^{-1} to that at 2367 cm^{-1} is less than about 3.6.

9. The article of claim 8 wherein the ratio of the absorbance of the copolymer at 982 cm^{-1} to that at 2367 cm^{-1} is less than about 3.4.

10. The article of claim 5 wherein the additional comonomer is perfluoro(propyl vinyl ether).

11. The article of claim 10 wherein the amount of perfluoro(propyl vinyl ether) is less than about 5% by weight.

12. The article of claim 1, 2 or 3 wherein the at least one additional comonomer is a mixture of hexafluoropropylene and perfluoro(propyl vinyl ether).

13. The article of claim 12 wherein the total amount of comonomers is less than about 8% by weight and the amount of hexafluoropropylene is less than about 6% by weight.

14. The article of any one of claims 1 to 13 wherein the melt-processible copolymer is fluorinated by treatment of the copolymer with fluorine, thereby providing a polymer substantially free of unstable end groups.

15. The article of claim 14 wherein the copolymer is treated with fluorine at a temperature above about 200°C but below the softening temperature of the copolymer.

16. The article of claim 2 or any claim when appendant thereto wherein the melt-processible copolymer is prepared by polymerization using an initiator which provides terminal -CF$_3$ groups.

17. The article of claim 17 wherein the initiator is selected from the group consisting of fluorine, difluorodiazine, perfluoroalkyl peroxides perfluoroacyl peroxides, perfluoroacyl hypofluorites, the reaction product of hexafluorpropylene trimers and fluorine, perfluoroacyl peroxides based on hexafluoropropylene oxide, difluoramines, perfluorazo compounds, perfluorosulfonyl azides, perfluoro acid chlorides, and perfluoroalkyl hypofluorites.

18. The article of any one of claims 1 to 17 wherein the article is a coaxial cable.

19. The article of any one of claims 1 to 18 wherein the copolymer is foamed.

20. A process for preparing a cable comprising a central conductor and a polymeric dielectric layer, which method comprises melt extruding around the central conductor a composition of a polymeric insulator consisting essentially of at least one melt processible copolymer of tetrafluoroethylene with at least one copolymerizable perfluorinated comonomer other than tetrafluoroethylene in an amount less than about 11.5% based on the weight of the copolymer and sufficiently low that the melting point of the copolymer is at least about 250°C, said copolymer being fluorinated at elevated temperature after polymerization.

21. The process of claim 20 wherein the polymer destined to be the insulator composition contains a foaming agent and the extrusion is conducted at a temperature such that the polymer expands after exiting the extrusion die, thereby providing a foamed polymeric insulator.

22. A process for preparing a cable comprising a central conductor and a polymeric dielectric layer, which method comprises melt extruding around the central conductor a composition of a polymeric insulator consisting essentially of at least one melt processible copolymer of tetrafluoroethylene with at least one copolymerizable perfluorinated comonomer other than tetrafluoroethylene in an amount less than about 11.5% based on the weight of the copolymer and sufficiently low that the melting point of the copolymer is at least about 250°C, said copolymer having substantially exclusively -CF$_3$ end groups, around a central conductor, and placing an out r conductive lay r around the polymeric insulator.

23. The process of claim 22 wherein the polymer destined to be the insulator composition contains a

foaming agent and the extrusion is conducted at a temperatur   such that the polymer expands after exiting th   extrusion die, ther by providing a foamed polymeric insulator.
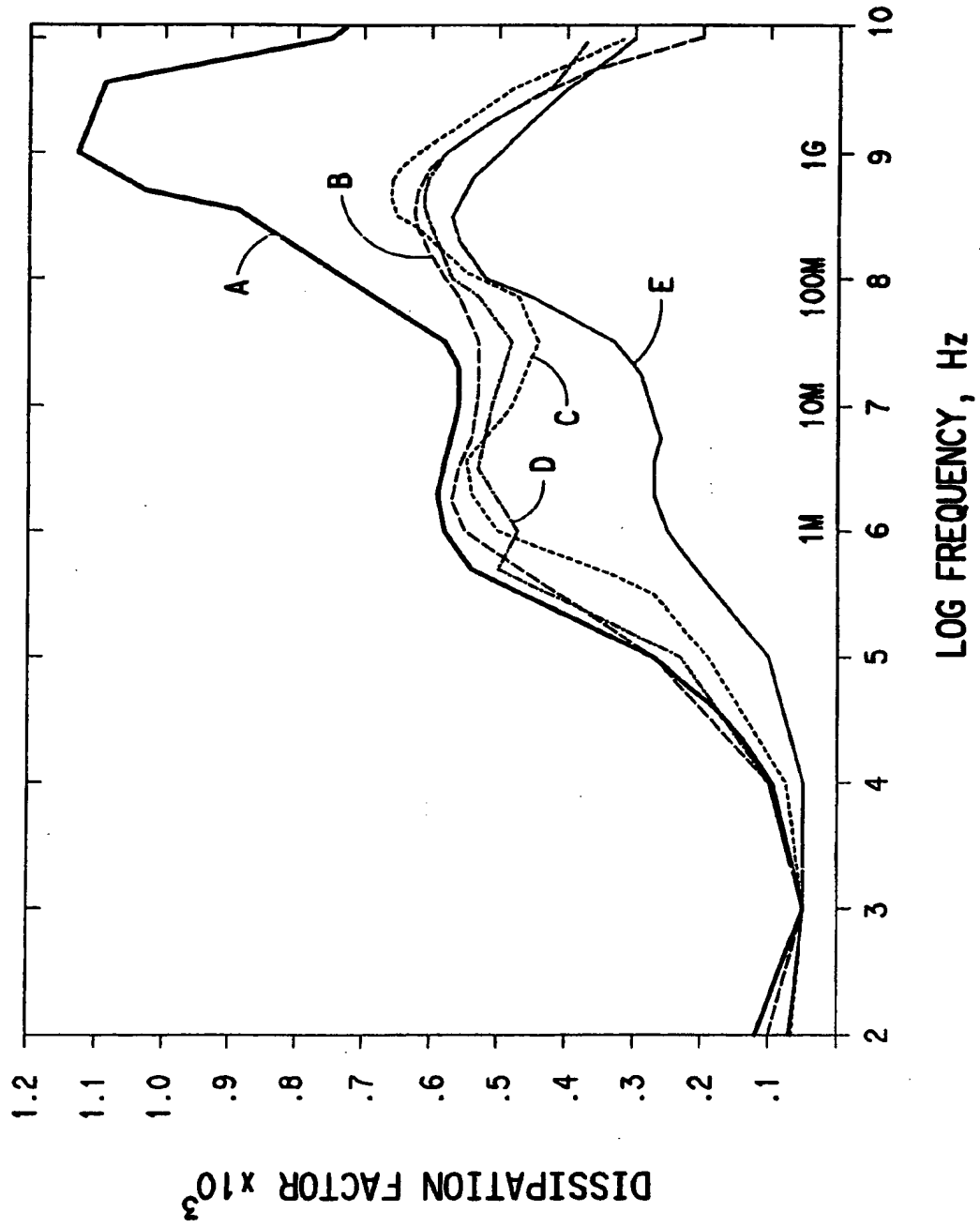
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FIG.1

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 220 910 (E.I. DU PONT DE NEMOURS AND COMPANY) ---		H 01 B 3/44 C 08 F 8/22
D,A	US-A-4 743 658 (J.F.IMBALZANO ET AL.) ---		
A	US-A-4 687 708 (K.BATZAR) ---		
D,A	US-A-4 626 587 (R.A.MORGAN ET AL.) ---		
D,A	GB-A-2 143 237 (RAYCHEM CORPORATION (USA-CALIFORNIA)) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

H 01 B
C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	18 February 91	PAULSSON R.L.